

Geologic Sequestration of CO₂: A Uniform Strategy for Assessing Mineralization Trapping Potential Across Rock Types

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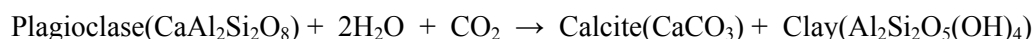
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Abstract

Dissolved CO₂ forms a weak acid that is neutralized by weathering subsurface minerals to produce carbonate and bicarbonate ions (alkalinity) and/or mineral carbonates. Of particular importance are weathering reactions involving silicate minerals rich in Ca, Mg and Fe. For example, the weathering of the calcic component of plagioclase feldspar (a common rock forming mineral) to calcite and a clay mineral can be written as



The thermodynamics for this reaction indicate that for any CO₂ pressure important for sequestration, the reaction will proceed as written, entombing the introduced CO₂ as solid calcium carbonate.

Mineralization potential will be highest in rocks with abundant Ca-, Mg-, and Fe-silicates (e.g., basalt) and lowest in rocks poor in these phases (e.g., sandstone). The time frame and extent of mineralization for a given subsurface environment (and hence its mineralization potential) are functions of the CO₂ induced weathering rates and the abundance of silicate phases.

In order to compare different rock types, we are developing a systematic assessment strategy that uses tabulated bulk chemical analyses of reservoir rocks to define normative mineralogical compositions for use in kinetic weathering calculations. A reaction path model and published kinetic rate laws are used to estimate the extent and time frame for mineralization trapping. Although the absolute results from this approach will not be adequate for accurate assessment of field scale entombment, they will allow the screening of a variety of rock types in a uniform and comparable manner. Results from the evaluation of deep basalt hosted aquifers in southern Idaho are presented to demonstrate our assessment approach.

Introduction

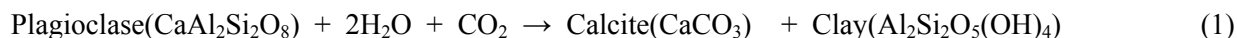
Carbon sequestration is one approach to stabilize or reduce the levels of greenhouse gases in the Earth's atmosphere. Geologic sequestration is the storage or entombment of CO₂ in subsurface geologic formations. Because approximately one third of the carbon dioxide emitted annually in the United States is from point sources, capture at the source coupled with geologic entombment has high potential to limit emissions. Potential geologic formations that may be conducive to sequestration include: deep saline aquifers, depleted oil/gas reservoirs, deep unmineable coal beds, and mafic/ultramafic rocks. Because many of these natural reservoirs are known to have stored fossil fuels and other fluids over geologic time frames, they can be expected to have high potential for the long-term sequestration of CO₂.

Geologic sequestration occurs via three interrelated processes. The first is hydrodynamic trapping where CO₂ is physically isolated by trapping beneath impermeable geological barriers such as a shale bed. This is the primary sequestering process in the short-term and is largely a function of the storage capacity of the deep system and its degree of isolation from the Earth's surface. The second process is solubility trapping in which CO₂ dissolves in subsurface fluids such as brines or petroleum. Solubility trapping is slower than hydrodynamic trapping and depends on the CO₂ dissolution rate in the fluid of interest. The third process is trapping due to mineralization in which CO₂ is entombed by increased weathering of the geochemically reactive base cations (primarily Ca²⁺, Mg²⁺, and Fe²⁺) in subsurface minerals. The weathering reactions result in the conversion of CO₂ into carbonate alkalinity and ultimately carbonate minerals. Because existing groundwaters are often saturated with carbonate phases, carbonate minerals formed from anthropogenic CO₂ will be permanently entombed in the subsurface. The time frame for mineralization trapping is primarily a function of the weathering rate and is much slower than the other two trapping processes. The permanence of sequestration by the three trapping processes is the inverse of their trapping time scale. Mineralization trapping offers the most permanent sequestration, hydrodynamic trapping the least. In an ideal sequestration site CO₂ would be permanently stored through presence of multiple trapping processes.

We are in the early stages of evaluating the geologic sequestration potential of sedimentary and volcanic basins in the Northern Rockies and Great Plains Region. This region includes Idaho, Montana, Wyoming and geologically contiguous areas in South and North Dakota. Ultimately the evaluation will explicitly consider hydrodynamic, solubility, and mineralization trapping at time scales at which these processes are important (tens to thousands of years). Uniform methods, applicable across varied rock types, are being developed for characterizing the potential of subsurface formations for CO₂ sequestration via solubility and mineralization trapping. Presented here is a summary of our assessment approach and preliminary results of its application to mixed volcanic and sedimentary sections of the Snake River Plain of southern Idaho.

Assessment Approach

Geologic sequestration will involve the injection of CO₂ captured from point sources into geologic formations as a supercritical fluid. The amount of CO₂ injected will exceed (in the short term) its solubility in the formation fluids (e.g., water) and will form a separate fluid-phase. Over time, the CO₂ will dissolve forming carbonic acid (H₂CO₃) that will be neutralized by weathering or corroding subsurface minerals to produce carbonate and bicarbonate ions (alkalinity) and/or mineral carbonates. Of particular importance are weathering reactions of silicate minerals rich in Ca, Mg and Fe. For example, the weathering of the calcic component of plagioclase feldspar (a common rock forming mineral) to calcite and a clay mineral can be written as:



Consideration of the thermodynamics of this reaction indicate that for any CO₂ pressure important for sequestration, the reaction will proceed as written, entombing the introduced CO₂ as solid calcium carbonate. Mineralization potential will be highest in rocks with abundant Ca-, Mg-, and Fe-silicates (e.g., basalt) and lowest in rocks poor in these phases (e.g., sandstone). The time frame and extent of mineralization for a given subsurface environment is a function of the silicate weathering rate and the abundance of appropriate silicate phases. The quantitative assessment of reaction (1) requires an understanding of the reaction rates and the abundance of the reactive phases. To address reaction rates, a generalized kinetic expression for mineral dissolution reactions that accounts for changes in pH was developed from results presented by Lasaga et al. (1994) and Drever (1997)

$$R = k_+ \cdot A \cdot \left(a_{\text{H}^+}^{0.5} + 10^{-3} + 10^{-5} \cdot a_{\text{H}^+}^{-0.25} \right) \left[1 - \frac{Q}{K} \right] \quad (2)$$

R	=	Reaction Rate
k_+	=	Forward Rate Constant
A	=	Reactive Surface Area
a_{H^+}	=	Aqueous hydrogen ion activity (pH)
Q	=	Ion Activity Quotient
K	=	Equilibrium Constant

Published kinetic information that can be used to derive k_+ is available for a limited set of minerals (e.g., Lasaga et al. 1994). Reactive surface area required in equation (2) can be estimated from geometric considerations or surface areas measured for whole rocks. The ion activity quotient can be calculated from water compositions. Equilibrium constants for a large number of minerals are available in published data bases (e.g., Bethke 2002).

In our assessment approach mineral precipitation reactions and reactions occurring in the water-rich fluid phase are assumed to be rapid when compared to dissolution reactions and were treated using equilibrium considerations. Reactions with the CO₂-rich fluid phase are ignored. The Geochemist's Workbench (v 4.03), a commercially available, mixed equilibrium-kinetics geochemical computer code (Bethke 2002) is used to model the weathering reactions that transform CO₂ to solid phase carbonate minerals.

Subsurface geologic formations are composed of a multitude of site (or rock type) specific minerals. Because kinetic data are available for only a limited subset of the possible minerals, an approach that transforms actual rock mineralogy to an idealized set of minerals that can be modeled is required. The

approach used here relies upon bulk whole rock chemical analyses for formation geomedial to calculate normative mineralogies. This approach provides a small, common-set of minerals that are independent of the site or formation being considered. Different sites and formations will differ only in their abundances normative minerals. Separate normalization approaches are being used for igneous (Lowenstern 2000) and sedimentary (Cohen and Ward 1991) rocks. For geochemical modeling, the normative mineralogy is simplified by removal of titanium and phosphorous containing phases. The use of normative mineralogies and geochemical modeling allows a uniform assessment of carbon sequestration potential for a variety of rock types. Although this approach will not accurately predict the capability for a given formation to sequester CO₂, it does not require site-specific kinetic data making it ideally suited for a regional survey of sequestration *potential* that includes a variety of rock types. The design of a sequestration system at a specific location should be guided by site specific models and mineralogies.

Application of Assessment Methodology to Volcanic Rocks of the Snake River Plain, Idaho

The carbon sequestration potential of hypothetical hydrocarbon plays in the Idaho-Snake River Downwarp Province (USGS 1995) will be evaluated as part of our regional assessment. The scenario considered for this paper was the direct injection of CO₂ into mafic-volcanic rocks. This scenario has applicability to 3 of the 4 Idaho-Snake River Downwarp plays that contain or are bounded by volcanic rocks.

Geology

The Idaho-Snake River Downwarp plays considered included the Pliocene Lake Idaho sediments and Columbia River Basalts, Miocene Lake Bruneau sediments and basalts, and Pre-Miocene sedimentary and volcanic formations (Figure 1). Maximum thickness for the different plays range from 2,100 to 3,000 meters. These plays are located within the eastern and western provinces of the Snake River Plain (SRP), in southern Idaho. The Eastern Snake River Plain (ESRP) and the Western Snake River Plain (WSRP) have been differentiated based on their geologic history and their hydraulic attributes. Structural evolution leading to the development of the ESRP and the WSRP began ~17 million years ago as the North American Plate moved southwesterly over the Yellowstone Hotspot, resulting in a volcanic province that becomes thinner and younger to the northeast (Barrash and Venkatakrishnan 1982). The ESRP is generally younger than the WRSP and is composed of volcanic rock (primarily basalt with lesser amounts of rhyolite) and relatively thin layers or lenses of sedimentary material that tend to thin towards the center of the basin. The ESRP is host to an extremely productive aquifer that flows through the fractured basalts in a southwesterly direction. The WRSP is a structural down warp that is believed to have been formed by crustal extension, beginning as early as 17 million years ago (Malde, 1991). Over the past 17 million years, this structural depression has been filled with basalt flows separated by thick lacustrine sequences (Figure 2).

Basalts of the Snake River Plain are dominantly olivine tholeiites consisting of approximately 50-60% labradorite, 40% augite, less than 10% olivine, and 5% glass (Kuntz et al. 1992). Iron-titanium oxides (mostly magnetite) and minor apatite also occur. Of this assemblage, the most reactive phases are mafic glass followed by silicic glass, olivine, pyroxene, oxides, and labradorite (Morse and McCurry 2002). Reactive minerals in the sedimentary interbeds include K-spar, clays, calcite, dolomite, quartz, and volcanic glass (Rightmire and Lewis 1987).

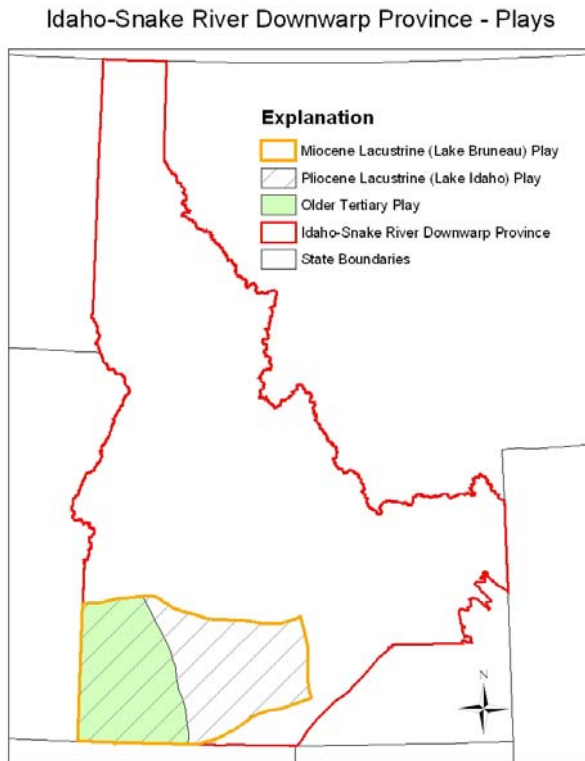


Figure 1. Map of Idaho showing locations of 3 plays (USGS 1995) with potential as carbon sequestration locations.

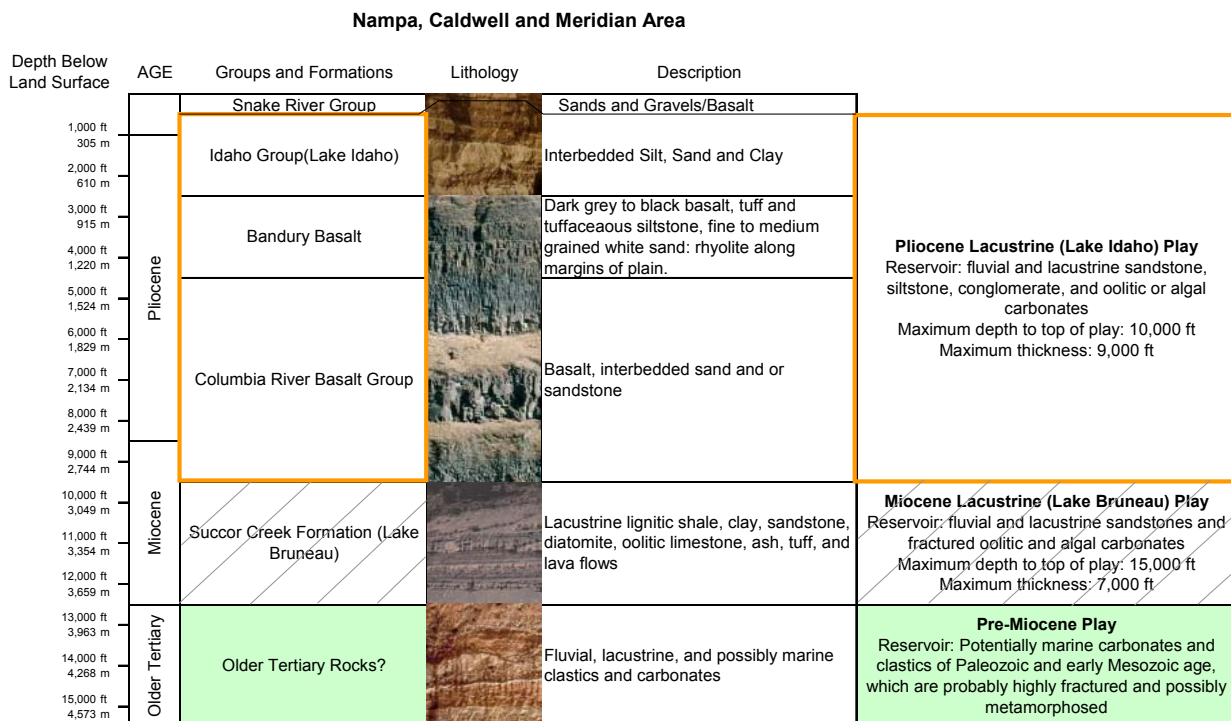


Figure 2. Generalized stratigraphic sections of Idaho plays with carbon sequestration potential.

Normative Media Properties

Average whole rock chemical composition for Snake River Plain basalts and the calculated normative mineralogy are given in Table 1. In addition to removing Ti- and P-bearing phases, in this example the iron silicate minerals were replaced by equimolar amounts of their Mg-counterparts. The minerals magnetite and ilmenite weather very slowly and are assumed to be inert on the time-scales considered for sequestration. Future analyses will explicitly consider iron-bearing phases. Specific surface areas for basalt phases are also given in Table 1 and were estimated from a total surface area calculated for the basalt and distributed among the normative mineral phases based on their volumetric abundances. The specific surface areas of the basalt was derived from geometric consideration with 1/3 of the porosity being attributed to 1 mm parallel fractures and 2/3 of the porosity attributed to intergranular porosity (assumed to be bundled capillary tubes with radius of 10.4 μm). A total porosity of 12.5% and median pore size of 10.4 μm was estimated from the averages of high pressure mercury injection tests conducted on 15 basalt samples.

Geochemical Modeling

The Geochemist's Workbench computer code was used to model the reaction of the normalized "rock" from Table 1 and a representative Snake River Plain groundwater. The geochemical model was 'calibrated' by adjusting the surface area to yield an estimated basalt reaction rate of 150 $\text{mg L}^{-1} \text{yr}^{-1}$ (Roback et al. 2001). Estimated specific surface areas were uniformly reduced by a factor of 100 to achieve calibration.

Using the calibrated model, a 500 year simulation for 200 bars CO_2 pressure and 40°C was conducted. Under these P-T conditions, hydrodynamic trapping for the basalt was approximately 29 kg m^{-3} if the full 12.5% porosity is occupied by supercritical CO_2 . As formation water reinvades the basalt, solubility and mineralization reactions will occur. Simplified results of the simulation showing solubility and mineralization trapping effects are shown in Figures 3 – 5. The simulation showed an initial dissolution rate of greater than 3 $\text{cm}^3 \text{L}^{-1} \text{yr}^{-1}$ (Figure 3). This rate decreased to a near steady-state rate of 1.5 $\text{cm}^3 \text{L}^{-1} \text{yr}^{-1}$ after approximately 75 years. As the rock dissolved, small amounts of clays and larger amounts of carbonates (Ca, Mg, Al) and zeolites formed (Figure 4). These alteration reactions resulted in a steady decrease in porosity with time, with approximately 1/2 of the original porosity remaining after 500 years. Because the simulation considered only chemical interactions and did not include multiphase fluid

Table 1. Average compositions of Snake River Plain Basalts (Kuntz et al. 1992) and calculated normative mineralogy and specific surface areas.

Oxides	Wt %	Normalized Mineralogy		Fe, Ti, P Free		Surface Area
			Wt %		Wt %	cm ² g ⁻¹
SiO ₂	46.10					
TiO ₂	2.60					
Al ₂ O ₃	14.51	Orthoclase (Or)	5.51	K-Feldspar	6.38	123
Fe ₂ O ₃	2.62	Albite (Ab)	20.89	Albite	24.24	120
FeO	10.57	Anorthite (An)	25.77	Anorthite	29.87	114
MnO	0.20	Diopside (Di)	17.09	Diopside	22.66	96
MgO	8.49	Hypersthene (Hy)	3.31			
CaO	10.34	Olivine (Ol)	16.64	Forsterite	16.85	98
Na ₂ O	2.47	Magnetite (Mt)	3.80			
K ₂ O	0.93	Ilmenite (Il)	4.93			
P ₂ O ₅	0.70	Apatite (Ap)	1.63			
Total	99.53	Total	99.55	Total	100.00	

flow, the full implications of porosity reduction on sequestration cannot be evaluated. Given that much of the porosity associated with basalts occurs as small intergranular pores, significant reduction in permeability may result from relative reductions in porosity of 30% or less. However, it appears that during early time (e.g. during injection), there was minimal porosity reduction suggesting that mineralization reactions may not reduce permeability during the operation lifetime of an injection well (a few years). At later time, mineralization reactions with their associated reduction in porosity may serve to seal and isolate formation fluids. Figure 5 shows the carbon sequestration potential of 1 m³ of basalt geomeadia. During early time this potential was dominated by hydrodynamic and solubility (initial 7.5 kg) trapping. Solubility trapping potential decreased with time primarily because of the reduction in porosity and a resulting decrease in the amount of fluid within the media. Mineralization trapping became more important than solubility trapping after about 140 years, and more important than hydrodynamic trapping after about 285 years. The total solubility and mineralization trapping potential for the basalt increased from 7.5 kg m⁻³ at time 0 to approximately 24 kg m⁻³ after 500 years. This value is on the same order as that of hydrodynamic trapping, suggesting that most of the injected carbon was sequestered via mineralization trapping.

Conclusions

The evaluations of the potential of geologic sequences for carbon sequestration potential need to consider the relative contributions of hydrodynamic, solubility, and mineralization trapping. The relative contribution to sequestration of these 3 processes will vary with rock type and time. In sequences that include basalts, such as those located in southern Idaho, all 3 processes contribute to sequestration, with hydrodynamic trapping import at early time and mineralization trapping dominating at later time.

Acknowledgement

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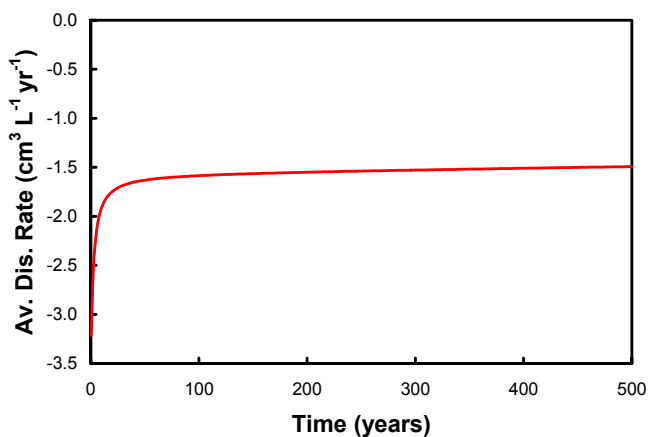


Figure 3. Calculated dissolution rate for basalt at 40°C and 200 bars CO₂ pressure.

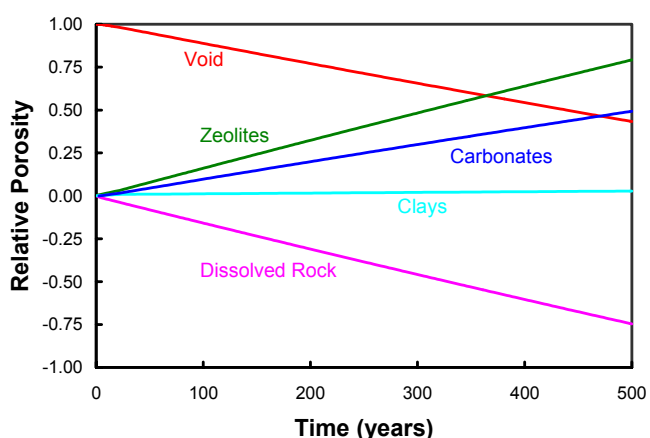


Figure 4. Generalized mineralogy and porosity changes for basalt reacting at 40°C and 200 bars CO₂ pressure.

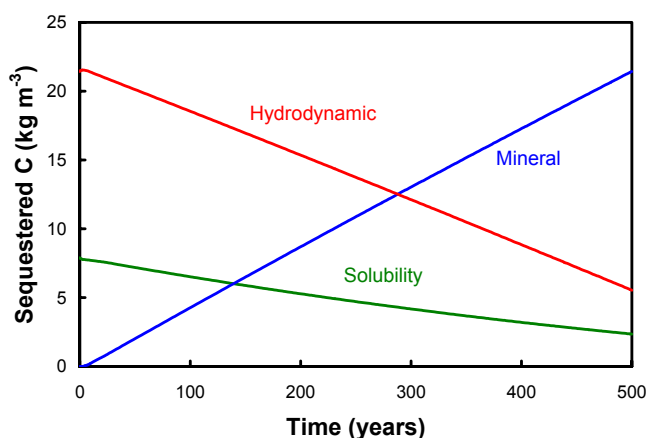


Figure 5. Contribution of hydrodynamic, solubility, and mineralization trapping to carbon sequestration potential of basalt at 40°C and 200 bars CO₂ pressure.